Preconcentration of low levels of americium and plutonium from waste waters by synthetic water-soluble metal-binding polymers with ultrafiltration

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A preconcentration approach to assist in the measurement of low levels of americium and plutonium in waste waters has been developed based on the concept of using water-soluble metal-binding polymers in combination with ultraflltration. The method has been optimized to give over 90% recovery and accountability from actual waste water.

We have previously demonstrated the use of watersoluble metal-binding polymers in combination with ultrafiltration as an effective method for selectively concentrating plutonium (Pu) and americium (Am) from dilute aqueous solutions.[1] This method uses water-soluble metal-binding polymers to selectively retain the metal ions of interest while unbound metal ions and salts pass through the ultrafilter with the bulk of the aqueous solution in the permeate or filtrate. This approach of using water-soluble metal-binding polymers has been in the literature for almost 30 years, but to date no practical application for waste waters has been reported for actinide preconcentration and measurement.[2] We have been developing this analytical separation/preconcentration technique for the determination of ultralow concentrations of alpha-emitting actinides from waste waters. The waste water streams tested were from the Radioactive Liquid Waste Treatment Facility (TA50), which receives acid and caustic aqueous waste water from most of the nuclear facilities at Los Alamos National Laboratory.

Experimental

Apparatus

In addition to the instruments and equipment previously sitedl the following were used: Matthews MDS-2000 microwave, stirred cell ultrafilters (Amicon, model 8200; Cole-Palmer, 25 mm and 76 mm model), cellulose acetate/polypropylene backed membranes (Amicon Disc Membrane YM10, 10,000 MWCO), and cellulose acetate sheets (Amicon) without the polypropylene backing. A CEiM Corp. germanium (lithium) detector connected to Ortec 919 SpectroMaster with Canberra Cryostat (model 750) was used.

Optifluor AF (Packard) was used for all scintillation counting. All chemicals used in the simulant and the 48-52% HF and 18-24% H_2SO_4 were Baker Analyzed reagent grade. The ion concentrations in the simulated waste water were based on the analysis of actual TA-50 waste. The simulated waste water ions and their concentrations are listed in Table 1. The spiked simulated waste water was prepared with 0.05 to 0.1% w/v polymer from prefiltered (0.2 μm filter) concentrate of the PPO_3H_2 (5% w/v) stock solution. The preparations of the various radioisotopes used in this study and the counting techniques were previously reported.[1] The preparation of the phosphoric acid polymer (PPO_3H_2) by reaction of formaldehyde and phosphorous acid with a polyamine was previously reported.[1,3,4]

Table 1. Composition of Simulated TA-50 Waste Water

Chemical species	Molar concentration	Reagents used
Ba^{2+}	$1.4 \cdot 10^{-7}$	$Ba(NO_3)_2$
Ca^{2+}	$2.9 \cdot 10^{-4}$	$Ca(NO_3)_2 \cdot 4H_2O$
Cl^{-a}	$1.1 \cdot 10^{-3}$	$NaCl$ ($CuCl_2$)
Cu^{2+}	$9.5 \cdot 10^{-7}$	$CuCl_2 \cdot 2H_2O$
F^-	$1.1 \cdot 10^{-4}$	NaF
Fe^{2+}	$4.6 \cdot 10^{-6}$	$Fe(NO_3)_2$
Mg^{2+}	$7.1 \cdot 10^{-5}$	$MgSO_4$
Ni^{2+}	$8.0 \cdot 10^{-5}$	$NiCl_2 \cdot H_2O$
Zn^{2+}	$1.9 \cdot 10^{-6}$	$Zn(NO_3)_2$
Nd^{3+}	$4.8 \cdot 10^{-9}$	$Nd(NO_3)_3 \cdot 6H_2O$
NH_3	$1.2 \cdot 10^{-4}$	NH_4OH
NO_2^-	$2.3 \cdot 10^{-6}$	$NaNO_2$
NO_3^{-b}	$1.1 \cdot 10^{-2}$	$NaNO_3$
PO_4^{3-}	$4.3 \cdot 10^{-6}$	Na_2HPO_4
K^+	$9.0 \cdot 10^{-4}$	KOH
Na^{+c}	$1.0 \cdot 10^{-2}$	$NaOH$

[a] Chloride from both $NaCl$ and $CuCl_2$.
[b] Present as zinc, calcium, and iron nitrate salts.
[c] Present from $NaCl$, NaF, $NaNO_3$, $NaNO_2$, and $NaOH$.

Procedures

Simulated waste water studies: A series of ultrafiltration experiments were performed with simulated TA-50 waste waters spiked with [241]Am(III) or [238]Pu(IV). The ultrafiltration experiments used a stirred cell apparatus pressurized with nitrogen to 75 psi. A measured volume of spiked solution was added to the cell

reservoir and stirred constantly during the ultrafiltration. Equal volumes of the retentate and permeate were analyzed for [241]Am by gamma spectroscopy and for [238]Pu by alpha liquid scintillation spectroscopy.

Spiked waste water studies: The experimental method for the simulated TA-50 waste water studies developed above required some additional modifications for actual TA-50 waste waters. The samples were treated with 2 ml of hydrofluoric acid per 1 of simulant solution to prevent silicate precipitation. The samples were then made 10^{-3} M in hydroxylamine-HCI for oxidation state adjustment to Pu(III), spiked with [241]Am or [238]Pu, adjusted to pH 4 with IM NaOH, and stirred for 2 hours in a water bath at 50°C. Ten ml of the 5% w/v stock solution of PPO_3H_2 was added to each liter of waste water sample, giving a 0.05% w/v polymer solution. The mixture was stirred for an additional 30 min. and added to the stirred cell to be filtered under 60 psi N_2 pressure. The filter apparatus was presoaked in 2M $NaNO_3$ to reduce adsorption on the cell reservoir surface and a cellulose acetate membrane, without the polypropylene backing, was used to aid in the subsequent membrane digestion. After filtration, the sides of the reservoir were rinsed with a 0.05% w/v PPO_3H_2 solution (pH 4) to remove any residual actinides adhering to the sides of the apparatus. Water-soluble polymer (final conc. 0.05% w/v) was again mixed with the permeate and the ultrafiltration repeated. The resulting permeate, retentate and membrane were then analyzed.

The permeate, retentate, and membrane were analyzed for actinide content as follows: I ml aliquot of permeate or retentate, and the folded membrane filter were placed in Roehen tubes and analyzed by gamma spectroscopy. We prepared any liquid samples for alpha liquid scintillation spectroscopy by combining 2ml aliquots with 16 ml scintillation fluid, and shaking the solution vigorously. The membrane filter was prepared for alpha liquid scintillation spectroscopy by dissolving the membrane in 1 ml of concentrated H_2SO_4 and diluting with DI water to 10 ml. A 2 ml aliquot of this solution was mixed with 16 ml of scintillation fluid and analyzed for [238]Pu. A retention percentage was calculated as 100% x [(retentate count in 1 ml x retentate volume) + (total membrane count)]/(starting material count in 1 ml x starting volume). Accountability was determined by summing all the components (membrane, retentate and permeate) and comparing it to the total starting solution activity.

Determination of gamma activity in raw waste waters by ultrafiltration: The procedure developed for the spiked TA-50 waste waters was used for the unspiked TA-50 waste waters. The 1 liter sample was ultrafiltered to dryness to concentrate the polymer/metal complex on the membrane. The membrane was placed in a counting tube and the complete sample analyzed by gamma-spectroscopy. In this way all the gamma-producing species that are concentrated from the solution could be measured without dilution effects.

To determine recovery and accountability, we carefully concentrated 100 ml of waste water to one ml in a plastic beaker using a heat lamp over 2 days. The 1 ml concentrate was measured by gamma-spectroscopy. The analysis measured the gamma-activity in the total waste water sample and was compared to the gamma-activity concentrated on the membrane from the ultrafiltration technique.

Results and discussion

PPO$_3$H$_2$ was chosen for these preconcentration experiments because its retention of ^{238}Pu and ^{241}Am was previously determined to be superior to commercially available polymers as well as other watersoluble metal-binding polymers reported in the literature.[1]

Simulated waste waters studies

Analytical methods development using ^{241}Am(III): Although the previously reported polymer evaluation work was performed on 2 ml samples,[1] preconcentration studies of waste water samples required large sample volumes. This factor necessitated the development of analytical procedures using larger-scale ultrafiltration equipment. In our earlier work[1] we had high accountability because we could measure both the sample and the sample container at the same time as there was no need for sample transfer. In these studies for analytical methods development on large samples (≥ 1 l) it was necessary to address the issues of quantitatively handling larger samples and sample transfer techniques.

The first approach was to treat a large volume of the sample to be analyzed (e.g., 1 l) by concentrating it to a small volume (e.g. 2 ml) using a stirred cell, and analyzing the concentrate radiochemically by gamma- or alpha-spectroscopy. This initial approach gave poor accountability. Analysis of all the filtration components in contact with the sample showed a high ^{241}Am content adhering to the membrane, often at levels higher than that found in the liquid retentate or concentrate. This finding was not unreasonable because a "cake" or concentration polarization layer of the soluble polymer forms on the membrane surface during the dead-end ultrafiltration process.[5] Thus, it was necessary to adjust the procedure and concentrate all the chelating polymer onto the ultrafiltration membrane surface by filtering to dryness. This adjustment allowed for complete desalting, cell reservoir washing, and acceptable accountability ($\geq 95\%$) of spiked ^{241}Am samples.

Low-level spiking studies of simulated waste water were performed to mimic the actinide levels found in the actual waste waters. Although this work proved to be good for procedural and technical development, the permeate counts were near the background level and it was difficult to obtain good accountability as shown in Table 2 for samples 1, 2, and 3. However, it should be noted that in each successive ultrafiltration (the permeate of the previous sample was treated with

fresh polymer and refiltered) that there was a measurable amount of ^{241}Am concentrated in the retentate. For the overall concentrate in three successive ultrafiltrations > 93% of the ^{241}Am was accounted for (total of samples 1, 2, and 3).

Table 2. Sequential Ultrafiltration of Simulate Waste Water with 0.05% w/v PPO$_3$H$_2$ and ^{241}Am(III) at pH 4

Sample number	Initial, cpm/ml	Initial volume, ml	Retentate, cpm	Permeate, cpm/ml	Permeate volume, ml	Retention, %
1[a]	171	300	44795	1	300	87.3%
2[a]	4	300	504	3	300	0.98%
3[a]	4	300	60	4	300	0.12%
4[b]	10,324	100	965,231	350	97	94.2%
5[c]	169	109	17,123	5	106	93.0%

[a] 93.3% for the total accountability of samples 1, 2, and 3
[b] 97.5% accountability.
[c] 96.1% accountability.

To overcome the accountability problem and obtain reliable counting data for ^{241}Am retention, studies were performed with higher activity levels. Sample 4 in Table 2 shows the experimental result for a higher spiking level of ^{241}Am. The higher radionuclide levels allowed for a more accurate measurement of the retentate and permeate and gave better accountability. Results indicate that ultrafiltration concentrates most of the polymeractinide complex on the first pass, leaving < 5% americium in the permeate. The recovery can be improved by using an additional polymer filtration step. This process involved adding 0.05% w/v PPO$_3$H$_2$ stock solution to the permeate, allowing it to stir for an additional 30 min, then ultrafiltering a second time. The first UF of sample 4 retained 94.2% of the ^{241}Am. Sequential treatment of the diluted permeate (sample 5) retained 93% of the remaining ^{241}Am. These results are important as similar percentages were retained on each sequential filtration even as the concentration of americium was significantly reduced. For analyses at ^{241}Am levels below the gamma detection limit of current instrumentation, we must assume that the same percentage of ^{241}Am will be retained for each polymer filtration step. This assumption is likely to be valid unless low concentrations of very strong molecular chelators are present to compete with the polymer and allow the complexed metal ion to pass through the ultrafilter.

The data for simulated waste waters (where exact concentrations and metal ion compositions are known) show that even at actinide metal-ion concentration of

10^{-8} M the polymer selectively bound ^{241}Am in the presence of calcium, magnesium, potassium, and sodium, which were present in much higher concentrations relative to ^{241}Am (Table 1). There was also selectivity for ^{241}Am(III) over divalent transition metal ions such as copper(II) and nickel(II) which were also present at much higher concentrations than Am(III). Iron(III) at a concentration >104 times higher than the ^{241}Am(III) did not interfere with ^{241}Am(III) binding at these tracer levels. In addition to the potential filling of binding sites by other metal ions, the polymer was competing with substantial concentrations of anions (phosphates and sulfates) for the actinide metal ion.

Another challenge encountered during these investigations was optimization of the ultrafiltration flow rates. Preliminary polymer solubility studies indicated that the PPO_3H_2 polymer was soluble under most conditions. In some runs an insoluble polymer cake layer retarded the filtration rate. This appears to result from batch-to batch variation of the synthesized polymer. Thus, a prefiltered polymer stock solution (5% w/v) was prepared and used in subsequent experiments, which resolved the problem. Precipitation was also observed at low pH values (<2) with the PPO_3H_2, but the precipitate redissolved on standing.

A filtration problem was encountered when real waste waters were used. When the sample was adjusted to pH 4 a gelatinous white material was produced, which greatly reduced the filtration rate. Los Alamos municipal water contains about 80 ppm of silicates. When acidified they precipitate as silicic acid, increasing the filtration time from hours to days. To overcome this problem, we treated the samples with a few drops of HF to convert the silicates to their fluorides, which do not precipitate. This treatment was combined with the oxidation state adjustment procedure.

Analytical methods development with ^{238}*Pu:* Spiking studies with ^{238}Pu(IV) indicated that even with the same precautions taken for ^{241}Am(III) to optimize the accountability and recovery (e.g., pH adjustment, washing, etc.), plutonium retention or concentration was low. When 1 l of waste water simulant was spiked with a ^{238}Pu(IV) stock solution, retentate recovery was only 34% (95% accountability) at pH 4 and a polymer concentration of 0.05% w/v. To enhance the chelating polymer binding of ^{238}Pu in the waste water, we adjusted the oxidation state to ^{238}Pu(III). The oxidation state adjustment of the ^{238}Pu(IV) spiking solution with either hydroxylamine or ascorbic acid increased total ^{238}Pu retention. Though the results for the two reductants were similar, the hydroxylamine worked slightly better (87% retention) than ascorbic acid (79% retention) and was used for subsequent experiments on real waste water. Although the binding of ^{238}Pu(IV) should be greater than ^{238}Pu(III) for the polymer, the ^{238}Pu(IV) can hydrolyze and polymerize even at pH 4 and also will potentially bind more strongly with other anions in the solution such as fluoride and phosphate. The ^{238}Pu(III) binds to the polymer with an affinity similar to ^{241}Am(III).

To analyze the membrane by alpha-scintillation spectroscopy it was necessary to dissolve the membrane. Using the unsupported cellulose acetate membrane and lowering the nitrogen pressure to 60 psi allowed us to obtain reasonable filtration rates of 0.3 l/hr without rupturing the membrane discs. The cellulose acetate membrane was easily dissolved in 1 ml of concentrated sulfuric acid and diluted to 10%, giving a solution which did not quench the plutonium alpha-spectrum or react with the scintillation cocktail.

Determination of low level gamma-activity in TA-50 outflow water: After completion of the developmental experiments on simulated and actual waste waters spiked with ^{241}Am and ^{238}Pu, ultra-low level analyses for total gamma-activity were performed on TA-50 outflow water. From duplicate samples 2 and 3, it can be seen from Table 3 that the initial gamma count is below detection limits since both the initial and permeate values are similar even though we were able to concentrate a measurable amount of gamma-activity in the retentate.

Table 3. Comparison of Ultrafiltration and Evaporation Preconcentration Approaches for TA-50 Outflow Waste Waters

Sample	Sample vol., ml	Initial, cpm/ml	Concentrate, cpm	Permeate, cpm/ml
1	100	7	31	-
2	1000	7	318	7
3	1000	2	314	6

It was very difficult to evaporate the 100 ml sample (sample 1, Table 3) because there were large amounts of solid that adhered to the vessel walls, the concentrated sample was quite viscous, and it required several days of careful evaporation to insure that there were no losses. Solids in this sample would also interfere with the technique of alpha counting by evaporation on a planchets, an analytical technique often used for lowlevel counting, because the solid residue blocks the alpha-particles. The presence of copious amounts of solids would also interfere with other analysis methods, such as ICP-MS or electroplating.

The results comparing two different preconcentration approaches indicated that the ultrafiltration method was successful. Using the same gamma detector for measurement of all samples, we saw an increase in the gamma-activity in the evaporated concentrate, sample 1, and the duplicate ultrafiltration samples 2 and 3. When 100 of TA-50 waste water was concentrated by evaporation (sample 1), 31 cpm/sample were obtained upon analyzing the complete sample. Thus, the normalized value for the evaporation procedure is 310 cpm/l which compares favorably to 318 and 314 cpm/l for the ultrafiltration method. The potential utility

of this preconcentration approach has been demonstrated by these results, but a rigorous analytical methods validation study is planned for future work.

Conclusions

A method has been developed for the analysis of ultra-low level ^{241}Am and ^{238}Pu in waste water by preconcentration through a polymer filtration technique. It consists of treating at least a one liter sample to adjust oxidation state, pH, and to stabilize silicate followed by addition of a water-soluble metal-binding polymer for actinide binding. ^{238}Pu and ^{241}Am are selectively retained and concentrated from the sample solution by ultrafiltration. The method has been optimized to give a 290% recovery and accountability of ^{241}Am and ^{238}Pu. Further optimization based on evaluating the effects of competing anions may be needed to improve ^{238}Pu recovery further. To increase the recovery of ^{238}Pu could require further optimization of the chelating polymer as opposed to the procedure. This analysis takes approximately 6 h (mostly unmanned), has very few steps, and does not produce mixed waste. The preconcentration method is potentially applicable to other methods of metal-ion analysis such as ICP-MS, plating, and alpha planchet counting as the samples are desalted. Some of these analytical methods can also determine isotopic distributions of the actinides which can often help to identify the source of the actinides, e.g., fallout or actinide processing operations. Further validation experiments to improve the statistics will be necessary along with evaluation of the retention of other actinides such as thorium, uranium, and neptunium.

Although this method was developed for preconcentration of waste water for improved analysis, a similar approach can be applied to waste water treatment to meet new discharge limits. The information obtained in these analytical studies will have direct applications to the development of waste treatment processes.

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